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Semivolatile behaviour and filter sampling artifacts for dicarboxylic acids during summer campaigns at three forested sites in Europe

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The sampling artifacts for C_2–C_5 dicarboxylic acids (DCAs) were studied by collecting high-volume $PM_{2.5}$ samples using front and back quartz-fibre filters. The filters were analysed for carbonaceous components, and for inorganic cationic and anionic and organic anionic species. Back/front filter ratios were determined for the C_2–C_5 DCAs, but also for methanesulphonate (MSA^-), the various inorganic species, and the carbonaceous components. The sampling artifacts for the inorganic species were small (< 5%) with the exception of those for nitrate. The median back/front filter ratios for MSA^- and the C_2–C_5 DCAs increased in the following order: oxalate (1.5%)–succinate (3%)–MSA^- (4%)–malonate (2%–9%)–glutarate (7%–26%). Most of these ratios are smaller than those that were obtained for organic carbon, total carbon, and especially water-soluble organic carbon. Our back/front ratios for the C_2–C_5 DCAs are lower to much lower than those found in other studies.

Introduction

Water-soluble dicarboxylic acids (DCAs) are among the most abundant organic constituents of atmospheric aerosols (e.g., Rogge *et al*. 1993) and they may affect the aerosols' hygroscopic and cloud-nucleating properties (Cruz and Pandis 1998, Peng *et al*. 2001, Abbatt *et al*. 2005). The DCAs originate from a multitude of anthropogenic and natural sources and result from both primary emissions and gas-to-particle conversion processes (e.g., Chebbi and Carlier 1996, Seinfeld and Pandis 1998, Legrand *et al*. 2005, Ray and McDow 2005). The relatively high concentrations of DCAs and their identification as atmospheric reaction products from a variety of different precursors make it useful to investigate their potential as indicators of secondary organic aerosol formation (Ray and McDow 2005).

DCAs are often sampled on quartz-fibre filters for subsequent off-line chemical analysis. However, it is well-known that the collection of carbonaceous aerosols on such filters is prone to both positive and negative artifacts. Many studies were concerned with assessing the sampling artifacts for organic carbon (OC) as a whole (e.g., Turpin *et al*. 2000, Mader *et al*. 2003, Salma *et al*. 2004, Subramanian *et al*. 2004, Viana *et al*. 2006a, 2006b, 2007, Schwarz *et al*. 2008, Vecchi *et al*. 2009) and occasionally studies were performed on the artifacts for water-soluble OC

(WSOC) (e.g., Viana *et al*. 2006a, 2007, Salma *et al*. 2007, Mkoma 2008, Chi 2009). However, it is rather rare that such studies are carried out on individual organic species. In the past decade, field studies on artifacts for low molecular weight (LMW) DCAs in quartz-fibre filter sampling were performed by Limbeck *et al*. (2001, 2005) and Ray and McDow (2005). Limbeck *et al*. (2001), and Ray and McDow (2005) made thereby use of a tandem filter setup (i.e., a setup with two quartz-fibre filters in series, i.e., Q1Q2). Limbeck *et al*. (2005) employed two approaches, i.e., on the one hand, a quartz-fibre filter, Teflon filter, and a second quartz-fibre filter (i.e., Q1TQ2) in series and, on the other hand, a TQ setup; both approaches were used at one of their two study sites and the latter approach only at the other study site. Negligible amounts of DCAs were found on the Teflon filters of the Q1TQ2 setup. In contrast, in all three studies substantial amounts of DCAs were found on the back quartz-fibre filter. The authors attributed the DCA concentrations on the back filter to the adsorption of gaseous organic species and concluded that the dicarboxylic acids have a semi-volatile behaviour. Ray and McDow (2005) also indicated that the sampling artifacts may depend on ambient temperature and relative humidity (RH) and that more research is needed to understand the behaviour of organic species sampling artifacts in other locations and under a wider variety of atmospheric conditions. In a recent study on gas/particle partitioning of LMW dicarboxylic acids (Bao *et al*. 2011) it was posed that the gas/particle partitioning of the DCAs not only depends on their concentration in the gaseous phase, but also on the characteristics of the atmosphere (e.g., temperature, sunlight and RH) and the aerosol (e.g., acidity, alkaline composition and water content).

Because of the apparent importance of artifacts when sampling with quartz-fibre filters in the studies of Limbeck *et al*. (2005) and Ray and McDow (2005) and because of the suggestions of Ray and McDow (2005) and of Bao *et al*. (2011) for more work on the subject, we employed a Q1Q2 setup in our summer sampling campaigns at three forested sites in Europe. Although the emphasis in our study was on the sampling artifacts for the DCAs, we also looked at the artifacts for various inorganic species.

Material and methods

Sampling sites

The three forested sites used in our study were K-puszta (Hungary), Brasschaat (Belgium), and Hyytiälä (Finland). K-puszta (46°58´N, 19°33´E, 136 m a.s.l.) is situated on the Great Hungarian Plain and is at 80 km southeast of Budapest (1.9 million inhabitants). The largest nearby town (Kecskemét, 110 000 inhabitants) is located 15 km southeast of the site. The sampling site is surrounded by forest (62% coniferous trees) interspersed with clearings. The aerosols collected here may be representative of forested rural background for the central-eastern European region. The site was selected as an air monitoring station by EMEP (European Monitoring and Evaluation Programme) and GAW (Global Atmospheric Watch) and is one of the 20 European supersites within the EU project EUSAAR (European Super-sites for Atmospheric Aerosol Research). More information on the site can be found in Ion *et al*. (2005), Ocskay *et al*. (2006), Pio *et al*. (2007), and Maenhaut *et al*. (2008a). The Brasschaat sampling site (51°19´N, 4°35´E, 15 m a.s.l.) is located within the state forest "De Inslag", a 78-year-old mixed pine-oak forest, in which the dominant tree species are *Pinus sylvestris* and *Quercus robur*. The site is at about 12 km northeast of the city centre of Antwerp (with a population of 500 000) and about 9 km to the east of the Antwerp harbour area; there is a major highway (E19/A1) to the south and in the south-east direction; the shortest distance between the sampling site and the major highway is about 1.5 km. So, local aerosols could be a mixture of anthropogenic emissions from the traffic, the city and harbour area of Antwerp, and biogenic emissions from the forest. Hyytiälä (61°51´N, 24°17´E, 181 m a.s.l.) is a forested site in southern Finland. It is a "Station for Measuring Forest Ecosystem–Atmosphere Relations" (SMEAR), i.e., SMEAR II, and like K-puszta one of the 20 European supersites within EUSAAR. The terrain around the station is representative of the boreal coniferous forest. This boreal coniferous forest station is relatively flat and the 40-year-old Scots pine (*Pinus sylvestris*) dominated stand is homogenous for about

200 m in all directions and extends 2–3 km in a north-northeast direction. There is a small lake located roughly 1 km to the west of the station. The largest city near the SMEAR II station is Tampere (200 000 inhabitants), which is about 60 km south-southwest from the sampling site. The major local aerosol emission is assumed to be of biogenic origin, but the local ambient air quality could be influenced by long-range transport of polluted air masses. Generally, it is a good site for studying the formation and characteristics of biogenic secondary organic aerosol (SOA) that is formed from biogenic volatile organic compounds (BVOCs). A detailed description of this site can be found elsewhere (Mäkelä *et al*. 1997, Kulmala *et al*. 2001).

Sampling campaigns and aerosol samplings

Two sampling campaigns were conducted at K-puszta (the first one in 2003, the second one in 2006), one in Brasschaat (in 2007), and one at Hyytiälä (also in 2007). All four campaigns were summer campaigns. In all campaigns, aerosol samples were collected with a high-volume dichotomous sampler (HVDS) (Solomon *et al*. 1983). This device separates the aerosol into fine [< 2.5 μm aerodynamic diameter (AD)] and coarse (> 2.5 μm AD) particles by means of virtual impaction. Both size fractions in the HVDS are collected on filters. The flow rate for the fine size fraction of our HVDS was about 300 l min^{-1} and that for the coarse size fraction about 34 l min^{-1}. Double 102-mm diameter Gelman Pall quartz-fibre filters (type 2500 QAT-UP), which had been pre-fired during 24 h at 550 °C, were used for both the fine and coarse size fractions. For the campaigns at K-puszta, the HVDS was set up on a platform at about 7 m above ground level; at Brasschaat it was installed on the first level of a tower at around 9 m above ground, and at Hyytiälä also on a tower at 14 m above ground level.

The 2003 campaign at K-puszta lasted from 4 June until 10 July. From the beginning of the campaign until the end of June, separate daytime (from about 07:00 to 18:30 local time, UTC + 2:00) and nighttime (from about 19:00 to 06:30 local time) samplings were performed, but from 1 July on, the collection time per sample was 24 h (with start at about 07:00 local time). A total of 63 actual samplings (27 daytime samplings, 28 nighttime samplings, and eight 24-h samplings) and 10 field blank samplings were made with the HVDS. The 2006 campaign at K-puszta lasted from 24 May until 29 June. Separate daytime and nighttime samplings were normally made, but there were also four 24-h samplings. The start and end times of the samplings were the same as in the 2003 campaign. A total of 68 actual samples (32 daytime samples, 32 nighttime samples, and 4 daily samples) and 9 field blanks were taken. The summer campaign at Brasschaat lasted from 5 June until 13 July 2007. Separate daytime (from about 07:15 to 20:15 local time, UTC + 2) and nighttime (from about 20:15 to 07:15) collections were normally made. A total of 71 actual samples (34 daytime samples, 34 nighttime samples, and three 24-h samples) and 10 field blanks were taken with the HVDS. The samplings in the campaign at Hyytiälä were done from 2 to 30 August 2007. They were normally done for separate day/night collections, with the daytime samplings from 07:30 to 19:40 local time (UTC + 3) and the nighttime samplings from 20:20 to 06:40 local time. There were a total of 51 actual samplings, which included 23 daytime samplings, 24 nighttime samplings, and four 24-h samplings, and of eight field blank samplings.

The actual filter samples and field blanks were stored in the freezer (at –25 °C) between sampling and analysis and the analyses were performed within two years after the sampling.

Meteorology and air mass origin during the sampling campaigns

Overall, the 2003 summer campaign at K-puszta was characterised by stable meteorological conditions (*see* Table 1). The weather was unusually warm and dry, and did not change significantly during the campaign. The daily maximum temperatures ranged from 24 to 36 °C. In contrast to the 2003 campaign, during the 2006 campaign, there was substantial variation in weather conditions (*see* Table 1). From a meteorological point

of view, this campaign could be divided into two periods. In the first (cold) period, which lasted from the start of the campaign until 11 June 2006, it was unusually cold with daily maximum temperatures 12–23 °C. For the remainder of the campaign (the warm period), it was warm with daily maximum temperatures from 24 to 36 °C, and the weather conditions were similar to those for the entire 2003 campaign. The air mass origin, as calculated with Hysplit (http://www.arl.noaa.gov/ss/models/hysplit.html; Lupu and Maenhaut 2002), was also quite different during the two periods of the 2006 campaign. For the cold period (24 May–11 June 2006), the air masses came from the north-west and often originated over the North Sea and/or the Atlantic Ocean. In contrast, for the warm period (12–29 June 2006), the air masses had essentially a continental character and they were more stagnant (Maenhaut *et al*. 2008a).

For the 2007 summer campaign at Brasschaat, the daily maximum temperatures ranged from 15 to 27 °C. During the first 10 days there was less rain, higher temperatures, and higher O_3 concentrations than during the remainder of the campaign, so that the levels of SOA were expected to be the highest in those days. As to the 2007 summer campaign at Hyytiälä, it remained fairly dry during the entire campaign. There were 14 days with rain throughout August (i.e., on 1, 3, 12, 15–19, and 26–31 August); most of these days, the total amount of rain was less than 4 mm; the only exceptions were 28 and 29 August with 8–9 mm. The mean daily temperature rose from 15 °C on 2 August to around 20 °C in the period 6–13 August and decreased down to 8 °C on 29 August, with a secondary maximum of 17 °C on 22–24 August. When excluding the last two days of the campaign, the daily maximum temperatures ranged from 15 to 27 °C. Incidentally, this range is very similar to that observed during the cold period of the 2006 campaign at K-puszta and identical to that for the campaign at Brasschaat. The air masses during the Hyytiälä campaign came mostly from the west, except in the period from 9 to 14 August, when they first showed a recirculation pattern on 11 and 12 August, and on 13 and 14 August they came from the south. During the period of 10–13 August there was extensive biomass burning in the southern part of European Russia, which considering the air-mass transport could have affected our measurements at the SMEAR II station (Maenhaut *et al*. 2011).

Chemical analyses

The front and back filters of the coarse and fine size fractions of the actual samples and of the field blanks were analyzed for OC, elemental carbon (EC), and total carbon (TC = OC + EC) with thermal-optical transmission (TOT) instruments from Sunset Lab (Birch and Cary 1996). The temperature protocol used was the UGent standard protocol. In this protocol, the temperature is raised up to 900 °C in both the first phase (in pure He) and in the second phase (in a He/O_2

Table 1. Summary of meteorological data for the four summer campaigns at the three forested sites, whereby the 2006 campaign at K-puszta is divided into two periods, i.e., cold and warm (*see* text).

Campaign[a]	Daily max. temp. range (°C)	Temperature (°C) Mean ± SD		Relative humidity (%) Mean ± SD	
		Daytime sampling	Nighttime sampling	Daytime sampling	Nighttime sampling
KP_Cold2006	12–23	16.9 ± 2.6	11.3 ± 2.4	59 ± 13	89 ± 7
KP_Warm2006	24–36	27.4 ± 3.1	18.5 ± 3.5	50 ± 7	89 ± 5
KP_2003	24–36	28.5 ± 3.1	19.0 ± 3.1	41 ± 11	77 ± 10
Brass_2007	15–27	18.0 ± 3.1	15.3 ± 1.9	72 ± 10	85 ± 7
Hyy_2007	15–27[b]	19.9 ± 2.7	14.9 ± 2.5	67 ± 10	84 ± 9

[a] KP stands K-puszta, Brass for Brasschaat, and Hyy for Hyytiälä.
[b] The last two days of the campaign were excluded in this range.

mixture) of the analysis. For more details on the OC/EC analyses, the temperature protocol, and the uncertainties that are associated with the OC and EC data, reference is made to Chi (2009).

Determination of WSOC was done by means of a Shimadzu TOC-V CPH high-sensitivity total organic carbon (TOC) analyzer. These analyses were only done for the front and back filters of the fine size fraction. Sections of the filters were extracted with Millipore Simplicity water, as described by Chi (2009). Water-soluble total carbon and inorganic carbon are measured separately. WSOC is obtained from the difference: WSOC = (total carbon) – (inorganic carbon). For more details on the WSOC measurements and the uncertainties that are associated with the WSOC data, reference is made to Viana *et al*. (2006a) and Chi (2009).

The front and back filters of the fine size fraction were subjected to ion chromatography (IC) analyses for water-soluble cationic and anionic species. These analyses were done with a combination of Dionex DX-600 and ICS-2000 instruments, whereby the first one was used for the anions and the latter for the cations. In both instruments, conductivity detection was used. The DX-600 is equipped with an EG40 KOH eluent generator, a continuously regenerated anion trap column (CR-ATC), and a carbonate removal device (CRD). Many inorganic and organic anionic species, including lactate, acetate, propionate, formate, methanesulphonate, valerate, keto-butyrate, chloride, nitrite, bromide, nitrate, benzoate, glutarate, succinate, malonate, maleate, sulphate, oxalate, phthalate, and phosphate, were looked for in the analyses with the DX-600. The columns used for most analyses were Dionex AG17 (or AG17-C) guard and AS17 (or AS17-C) analytical columns (all of 2 mm diameter), and the autosuppressor was an ASRS-ULTRA II (2 mm) operating in the external water mode. The eluent for most analyses consisted of a KOH gradient with concentration going from 0.4 mM to 30 mM and with a duration of 30 min (+4 min for initialisation/equilibration). The eluent flow rate used with this program was 0.45 ml min^{-1} and the suppressor current was kept at 100 mA. For the HVDS samples from the 2003 campaign at K-puszta different columns (i.e., AG11 and AS11) and a somewhat different gradient program was used (Kourtchev *et al*. 2009). The Dionex ICS-2000 was used for measuring the cationic species (i.e., Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}). An EG50 methanesulphonic acid eluent generator was employed to generate the isocratic eluent (21.5 mM methanesulphonic acid). The columns used were Dionex IonPac CG12A guard and CS12A analytical columns (both of 2 mm diameter), and the autosupressor was a CSRS-ULTRA II (2-mm), used in the recycle mode. The eluent flow rate was 0.25 ml min^{-1}. The injection valve of the ICS-2000 is connected with that of the DX-600, so that the analyses for both cations and anions are done with a single injection. The volume of the injection loop was 100 μl in the DX-600 system and 25 μl in the ICS-2000 system. The data acquisition and analysis software used with the combined DX-600 and ICS-2000 instruments is Chromeleon. For the IC analyses, a section of 3 or occasionally 1.5 cm^2 (for the front filters) or of 6 cm^2 (for the back filters) was inserted in a polystyrene tube of 15 ml and 5 ml (or exceptionally 10 ml) Millipore Simplicity water was added. The tube was vigorously hand-shaken for 5 min and then allowed to stand for about 30 min. The aqueous extract was then taken with a 10-ml pipette and filtered through a 25-mm diameter pre-cleaned syringe-filter (HPLC Syringe Filter, PVDF, 0.2 μm pore size, Alltech Associates Inc.) and the filtrate was taken up in a clean 15-ml polystyrene tube. All IC analyses were done with manual injection. About 0.6 ml was pipetted from the filtered aqueous extract with a 1 ml syringe and injected into the injection valve of the ICS-2000 through a 13-mm-diameter syringe filter (PVDF, 0.22 μm pore size, Millipore Corporation). All analyses of the filtered extracts were done in duplicate whereby the second injection and analysis was, on average, done at around 3 h after the first injection and analysis. Between the two injections, the tube with the filtered extract was kept in the refrigerator. For quantification for the various species, net peak areas, as obtained with the Chromeleon software, were used. Calibration curves were constructed every few weeks by injecting from a series of standard solutions. On each analysis day, also two injections of an appropriate control standard were made (one at

the start and one at the end of the analysis day). Further details on the IC analyses and on the associated uncertainties and the detection limits can be found in Wang (2010).

All concentration data were corrected for field blanks, whereby averages were made over the field blanks per campaign.

Results and discussion

Intercomparison of the HVDS $PM_{2.5}$ front filter data from the three forested sites

The data from the $PM_{2.5}$ front filters of the HVDS samples from the various campaigns are compared with each other in Table 2. In the table and also in the text below, the organic acids are for simplicity denoted as salts (e.g., oxalate), but as indicated by Yang and Yu (2008), IC analyses, as done by us, actually measure the sum of the acidic and anionic forms of the species (e.g., of oxalic acid + oxalate), including partially and fully dissociated DCAs. As indicated earlier, the anion analysis column was different for the samples from the 2003 campaign at K-puszta than for the other campaigns. With the AS11 column used for the 2003 campaign, malonate was not well separated from other species. Therefore, no malonate results are given for that campaign.

The highest OC concentrations were obtained in the 2003 campaign and the warm period of the 2006 campaign at K-puszta, then followed by the 2007 campaign at Hyytiälä (Table 2). The ambient temperatures were highest in the 2003 campaign and the warm period of the 2006 campaign (*see* Table 1). As a consequence, emissions of BVOCs and likely also their conversion into SOA were enhanced (Maenhaut *et al*. 2008a). However, the contribution from organic matter to the $PM_{2.5}$ mass was highest at Hyytiälä, as there were low concentrations of secondary inorganic aerosol (SIA) and mineral dust at this site (Wang 2010, Maenhaut *et al*. 2011). EC was

Table 2. Intercomparison of HVDS data: Median concentrations and interquartile ranges (in ng m^{-3}) for TC, OC, EC, WSOC, MSA^-, DCAs, and water-soluble inorganic species, as derived from the PM2.5 size fraction front filters of the HVDS samples from the cold and warm periods of the 2006 summer campaign and the entire 2003 summer campaign at K-puszta, and from the 2007 summer campaigns at Brasschaat and Hyytiälä. Also included in the table are the mean percentages and associated standard deviations of the WSOC explained by the carbon in the sum of MSA^- and the 4 DCAs.

Species	K-puszta 2006, Cold period (n = 33)	K-puszta 2006, Warm period (n = 34)	K-puszta 2003 (n = 63)	Brasschaat 2007 (n = 71)	Hyytiälä 2007 (n = 51)
TC	2100 (1730–2500)	4600 (3700–5300)	4400 (3300–4900)	2100 (1660–2800)	2600 (1650–3400)
OC	1960 (1540–2300)	4500 (3400–4900)	4200 (3100–4700)	1730 (1270–2200)	2400 (1540–3300)
EC	143 (124–192)	176 (130–250)	195 (151–240)	400 (280–620)	164 (101–191)
WSOC	970 (770–1130)	2900 (2200–3200)	2600 (1710–3000)	810 (570–1170)	1570 (870–2100)
NH_4^+	840 (580–1040)	1530 (1130–2000)	1520 (1190–2100)	1080 (650–2100)	520 (280–1880)
SO_4^{2-}	1790 (1170–2400)	3600 (2600–4400)	3500 (2800–4400)	2700 (1840–3900)	1640 (930–2300)
NO_3^-	410 (300–750)	360 (197–500)	310 (230–420)	650 (400–2200)	71 (45–106)
Cl^-				40 (15.7–93)	
Na^+	30 (13.8–47)	35 (22–51)	48 (32–66)	108 (65–210)	55 (35–84)
Mg^{2+}	2.3 (1.14–3.9)	6.8 (4.6–13.8)	14.7 (10.3–18.9)	2.7 (1.42–6.7)	3.5 (1.91–5.0)
K^+	48 (39–810)	81 (64–127)	67 (47–83)	38 (18.7–93)	47 (14.2–77)
Ca^{2+}	22 (14.5–320)	88 (57–210)	198 (151–250)	27 (14.7–36)	22 (15.1–37)
MSA^-	29 (12.2–44)	29 (22–36)		79 (46–119)	45 (31–58)
Oxalate	73 (56–85)	210 (154–250)	196 (138–230)	75 (50–140)	104 (67–132)
Malonate	33 (24–37)	65 (50–76)		49 (28–82)	19.7 (10.0–33)
Succinate	32 (26–38)	142 (100–166)	41 (26–51)	11.0 (5.7–54)	12.6 (4.4–23)
Glutarate	7.1 (4.9–9.0)		7.8 (5.5–11.7)	4.7 (3.3–9.7)	7.0 (5.0–8.8)
∑(MSA^- + DCAs)C% of WSOC	5.3 ± 0.9	5.0 ± 0.6	2.9 ± 0.4	8.0 ± 3.0	3.1 ± 1.0

highest at Brasschaat, which is due to the influence of nearby traffic emissions.

As to the measured organic anions, methanesulphonate (MSA^-) has a different origin than the four DCAs. MSA^- is a gas-to-particle conversion product of dimethylsulphide (DMS), which is itself emitted by marine phytoplankton (e.g., Saltzman *et al*. 1983, Kettle and Andreae 2000). Consequently, the MSA^- concentrations in ambient air are strongly affected by maritime air masses; the closer the sampling site is to seas or oceans with high primary productivity, the higher the MSA^- concentrations may be. Since the Brasschaat site is closer to the sea than the other two forested sites, the highest MSA^- concentrations are noted at this site. As indicated in the Introduction, the DCAs originate from a multitude of anthropogenic and natural sources and result from both primary emissions and gas-to-particle conversion processes. Of the four DCAs measured, oxalate was the most abundant one and it exhibited its highest concentrations during the warm periods at K-puszta; it accounted for at least 50% of the sum of the 4 DCAs. At rural sites with little anthropogenic impact, a high contribution from oxalate to the sum of the DCAs points to aged organic aerosol. Malonate was the second most abundant DCA at Brasschaat and Hyytiälä, while succinate outweighted malonate during the warm period of the 2006 summer campaign at K-puszta. Glutarate provided the lowest contribution to the DCAs at all three sites. This result is in agreement with those found at other clean sites (e.g., Kawamura *et al*. 1996, 2001, Legrand *et al*. 2005).

As can be deduced from the sea-salt and sulphate data given in the recent European aerosol phenomenology paper of Putaud *et al*. (2010), fine SO_4^{2-} is within Europe for 90% or more nss-SO_4^{2-}. The latter is essentially due to gas-to-particle conversion of anthropogenic SO_2; its concentration can therefore be used as an indicator of the pollution situation. At Hyytiälä, the SO_4^{2-} concentrations were lower than at the other two forested sites, indicating that that site was the cleanest. NO_3^- is useful to estimate the impact of traffic or other high-temperature combustion processes; the rather low median concentration (71 ng m^{-3}) at Hyytiälä indicates that there was little impact from fossil fuel combustion at this site; in contrast, the relatively high median of 650 ng m^{-3} for Brasschaat hints to a large influence from traffic emissions at this site. As was the case for SO_4^{2-} and NO_3^-, also for NH_4^+ the lowest median concentration (520 ng m^{-3}) is noted at the Hyytiälä site. The highest median concentrations for the sea-salt ions Na^+ and Cl^- were observed at Brasschaat, which is explained by the shortest distance from the sea. The highest median concentrations of Mg^{2+} and Ca^{2+} were observed at K-puszta (i.e., in the 2003 campaign and the warm period of the 2006 campaign). Their high levels are explained by the high concentrations of mineral dust as a result of drier soils and possibly also increased agricultural activities in warm weather (Maenhaut *et al*. 2008a, 2008b).

Extent of neutralisation of the $PM_{2.5}$ aerosol

As indicated above, DCAs and MSA^- are measured in our IC as the sum of their acidic and salt forms. Within the aerosol, they could be present as acids, as salts or as a mixture of both, depending upon the pH or acidity of the aerosol. Oxalic acid is the strongest acid of the 4 DCAs measured by us, with pK_{a1} = 1.25 and pK_{a2} = 3.81 (Lide 2006), followed by malonic acid (pK_{a1} = 2.85; pK_{a2} = 5.70), succinic acid (pK_{a1} = 4.21; pK_{a2} = 5.64), and glutaric acid (pK_{a1} = 4.32; pK_{a2} = 5.42). Oxalid acid should therefore have a higher proportion of the salt form in the aerosol than the other (weaker) DCAs. Yang and Yu (2008) measured both the acidic and salt forms for the C_2 and C_3 diacids in Singapore and found, in accordance with the above, that the concentrations of oxalate were 10–15 times higher than those of oxalic acid, whereas the concentrations of malonate were no more than half of those of malonic acid. They estimated that the collected ambient particles in their study contained a pH ranging from 2.2 to 2.5.

In order to obtain an idea of the acidity of our aerosol samples, we calculated the ionic balance in terms of equivalent ratios between the cations and anions measured for the $PM_{2.5}$ front filters. Three different ratios were calculated, i.e., first, the ratio of the sum of all cations (in equivalents) to the sum of all inorganic anions (in equivalents),

secondly, the ratio of the sum of all cations to the sum of both the inorganic and organic anions, and third, the ratio of the sum of all cations to the sum of both the inorganic and organic anions plus Mg and Ca. As carbonates and bicarbonates were not measured in our IC analyses and may be important anionic species in the aerosol (usually associated with Ca and Mg), the sum of the Mg and Ca equivalents was used as an upper estimate for the carbonate and bicarbonate equivalents. Ratios were also calculated for the separate daytime and nighttime samplings of each sample set, but their averages were very similar (all within 1%) to the overall averages (*see* Table 3).

The acidic species in our $PM_{2.5}$ aerosol samples were fairly well neutralised at K-puszta and Brasschaat and to somewhat lesser extent at Hyytiälä (*see* Table 3). It is therefore thought that oxalic acid may mainly have been present as oxalate in our samples and not so much as free acid. Also malonic acid and perhaps even succinic and glutaric acid could to a substantial extent have been present as salts. Consequently, much less of the DCAs is expected to be in the vapour phase than if they would have been present as free acids in the aerosol. NH_4^+ played a very important role in the neutralisation of the acidic species, as it accounted, on average, for between 80 and 90% of the summed cation equivalents in the various sample sets.

Overall back/front filter ratios for $PM_{2.5}$ in our sample sets and comparison with literature data

In comparing with the literature data (*see* Table 4), it should be taken into account that there were substantial differences in sampling conditions and types of sites. The quartz-fibre filters used in the three earlier studies were, as in our case, pre-fired and Limbeck *et al*. (2001, 2005) made use of the same filter type as we did (i.e., Pallflex 2500 QAT-UP); Ray and McDow (2005) did not specify their filter type. Limbeck *et al*. (2001) did their aerosol samplings in spring/summer at a savanna site in South Africa. They made use of a low-volume TSP tandem filter (Q1Q2) sampler with 47-mm diameter filters, the air face velocity for the filters was 22 cm s^{-1} and the collection time per sample was 1 week. Low-volume TSP samplers with 47-mm diameter filters were also used in the study of Limbeck *et al*. (2005) and samplings were performed at two sites, i.e., an urban site (Vienna) and a continental background site (Mt. Rax, Austria, 1644 m a.s.l.). The samplings at Vienna were done in winter, first with a Q1TQ2 setup for 36 h per sample and subsequently with a TQ setup between 7.5 and 24 h per sample. The samplings at Mt. Rax were performed in spring and with the TQ setup; the collection time per sample varied from 7 to 13 h. The face velocity with both the Q1TQ2 and TQ setups was 51 cm s^{-1}. Ray and McDow (2005) made use of a Anderson high-volume PM_{10} sampler and collected separate day and night samples during a summer campaign. The face velocity with their sampler was 44 cm s^{-1}. For comparison, the face velocity for $PM_{2.5}$ in our HVDS tandem filter samplings was 80 cm s^{-1}, and the collection time per sample was typically 12 h. None of the three studies referred to provided information on the acidity of the aerosol samples or data to assess it.

As far as the inorganic cations are concerned, all our back/front filter ratios are low (with medians between 0 and 0.06), with the exception of these for NH_4^+, K^+, and to a lesser extent also Na^+

Table 3. Equivalent ratios of cations/inorganic anions, cations/all anions, and cations/all anions + Mg + Ca in the different campaigns. Values are means ± SDs.

Campaign[a]	Cations/inorg. anions	Cations/all anions	Cations/all anions + Mg + Ca
KP_Cold2006	1.06 ± 0.05	0.99 ± 0.05	0.96 ± 0.06
KP_Warm2006	1.22 ± 0.07	1.10 ± 0.06	1.01 ± 0.07
KP_2003	1.27 ± 0.08	1.20 ± 0.08	1.05 ± 0.08
Brass_2007	1.04 ± 0.10	0.98 ± 0.10	0.96 ± 0.10
Hyy_2007	1.04 ± 0.07	0.95 ± 0.07	0.91 ± 0.07

[a] KP stands K-puszta, Brass for Brasschaat, and Hyy for Hyytiälä.

Table 4. Medians and interquartile ranges for the back/front filter ratio of TC, OC, EC, WSOC, MSA^-, DCAs, and water-soluble inorganic species, as derived for the PM2.5 size fraction filters of the HVDS samples from the various campaigns. Comparison with averages for the back/front ratio given in the literature.

Species	K-puszta 2006, cold period (n = 33)	K-puszta 2006, warm period (n = 34)	K-puszta 2003 (n = 63)	Brasschaat 2007 (n = 71)	Hyytiälä 2007 (n = 51)	Limbeck *et al.* (2001)	Limbeck *et al.* (2005) Q1TQ2 Vienna	Limbeck *et al.* (2005) TQ Vienna	Limbeck *et al.* (2005) TQ Mt. Rax	Ray & McDow (2005)
TC	0.14 (0.09–0.17)	0.14 (0.12–0.16)	0.11 (0.10–0.13)	0.13 (0.12–0.16)	0.15 (0.13–0.19)	0.12				
OC	0.16 (0.10–0.18)	0.15 (0.12–0.17)	0.12 (0.10–0.13)	0.17 (0.15–0.20)	0.16 (0.14–0.20)					
EC	0.00 (0.00–0.00)	0.00 (0.00–0.00)	0.00 (0.00–0.01)	0.00 (0.00–0.00)	0.00 (0.00–0.00)					
WSOC	0.23 (0.17–0.26)	0.17 (0.13–0.19)	0.19 (0.15–0.19)	0.21 (0.18–0.25)	0.17 (0.11–0.28)					
NH_4^+	0.10 (0.05–0.16)	0.00 (0.00–0.00)	0.02 (0.01–0.03)	0.04 (0.00–0.07)	0.00 (0.00–0.01)					
SO_4^{2-}	0.00 (0.00–0.00)	0.00 (0.00–0.00)	0.01 (0.00–0.01)	0.00 (0.00–0.00)	0.00 (0.00–0.00)	0.017				
NO_3^-	0.54 (0.44–0.68)	0.29 (0.18–0.36)	0.26 (0.17–0.28)	0.24 (0.15–0.34)	0.25 (0.13–0.36)					
Cl^-				0.26 (0.14–0.48)						
Na^+	0.07 (0.00–0.19)	0.01 (0.00–0.08)	0.06 (0.02–0.08)	0.01 (0.00–0.05)	0.00 (0.00–0.06)					
Mg^{2+}	0.00 (0.00–0.00)	0.00 (0.00–0.00)	0.04 (0.01–0.04)	0.00 (0.00–0.00)	0.00 (0.00–0.00)					
K^+	0.23 (0.07–0.35)	0.00 (0.00–0.09)	0.03 (0.00–0.04)	0.04 (0.00–0.22)	0.00 (0.00–0.00)					
Ca^{2+}	0.00 (0.00–0.00)	0.00 (0.00–0.00)	0.05 (0.02–0.06)	0.00 (0.00–0.01)	0.00 (0.00–0.00)					
MSA^-	0.04 (0.01–0.11)	0.03 (0.01–0.08)		0.03 (0.01–0.08)	0.06 (0.02–0.10)					
Oxalate	0.02 (0.01–0.02)	0.01 (0.01–0.03)	0.02 (0.01–0.03)	0.01 (0.01–0.01)	0.01 (0.00–0.02)	0.14	0.06	0.30	0.11	
Malonate	0.06 (0.03–0.13)	0.03 (0.01–0.13)		0.02 (0.00–0.04)	0.08 (0.02–0.17)	0.013	0.009	0.06	0.08	0.45
Succinate	0.04 (0.02–0.08)	0.03 (0.01–0.05)	0.03 (0.01–0.03)	0.02 (0.00–0.10)	0.02 (0.01–0.06)	0.26	0.16	0.55	0.41	0.15
Glutarate	0.25 (0.17–0.35)		0.21 (0.15–0.23)	0.26 (0.17–0.42)	0.07 (0.00–0.15)	0.38	0.36	0.78	0.81	0.35

in our 2003 K-puszta samples. There were serious problems with the blank correction for the cations in the samples from this first campaign, and this may at least in part explain those higher ratios. As to the inorganic anions, our back/front ratios were very low for SO_4^{2-} (all medians are in the range 0–0.01); Also Limbeck *et al*. (2001) found a very low average ratio of 0.017 for this species. For NO_3^- and Cl^- very substantial back/front ratios were obtained by us, which are clearly indicative of sampling artifacts. Artifact-free sampling of particulate NO_3^- is not simple because of possible adsorption of gaseous HNO_3 by the filter and volatilisation of particulate NH_4NO_3 from the filter (e.g., Schaap *et al*. 2004, Wieprecht *et al*. 2004, Vecchi *et al*. 2009). As to artifacts for Cl^-, these are well-documented, especially for marine and coastal aerosols, and are due to adsorption of HCl and loss of Cl from the filter by reaction of NaCl and other chlorides with acidic gases and particulate acidic species (e.g., Graedel and Keene 1995, Pio and Lopes 1998).

With regard to the carbonaceous components, our median back/front ratios were very low for EC, as expected for a component which is only present in the particulate phase and exhibits no volatility. In contrast, for OC (and also TC), substantial back/front ratios were obtained. Our data for OC are more or less in line with those found in many earlier studies (e.g., Turpin *et al*. 2000, Mader *et al*. 2003, Salma *et al*. 2004, Subramanian *et al*. 2004, Viana *et al*. 2006a, 2006b, 2007, Schwarz *et al*. 2008, Vecchi *et al*. 2009), although higher ratios were observed in some of these studies. The OC on the back filter is thought to be mainly due to adsorption of volatile organic compounds (VOCs) (e.g., Turpin *et al*. 2000, Mader *et al*. 2003). As to TC, which consists at our sites for 80% or more of OC (Table 2), Limbeck *et al*. (2001) found back/front filter ratios that are similar to ours. Our back/front filter ratios for WSOC are all systematically larger than those for OC. Salma *et al*. (2007) found the same phenomenon at a kerbside in Budapest. Their explanation was that the organic compounds that are mainly responsible for the adsorptive sampling artifacts seem to be more water-soluble; thus they possibly contain more polar functional groups or they may be more oxidized than the organic matter in general. They stated that this is in agreement with the expectation that quartz-fibre filters primarily adsorb polar (thus more water-soluble) organic molecules, while the volatile or semi-volatile organic compounds are often non-polar. They also found that the back-to-front ratios for the WSOC were strongly and negatively correlated with the WSOC concentration, $PM_{2.5}$ mass concentration, and ambient temperature.

Our back/front ratios for MSA^- are all small (medians from 0.03 to 0.06). Considering the extent of neutralisation of our aerosol and the fact that methanesulphonic acid is a strong acid, this species is expected to be mainly present as salt instead of as free acid. Thus, although the vapour pressure of the acid is 0.075 Pa (Tang and Munkelwitz 1991) and much larger than the vapour pressures of the DCAs (given below), artifacts originating from the semi-volatility of the acid are expected to be small for our samples.

As to the DCAs, our median back/front filter ratios for oxalate are in the range of 0.01 to 0.02 and clearly lower than the average ratios of 0.06 to 0.30, which were obtained in the studies of Limbeck *et al*. (2001, 2005). For malonate, our ratios (medians in the range of 0.02 to 0.08) are similar to those obtained by Limbeck *et al*. (2001, 2005), but a much larger ratio (mean of 0.45) was obtained by Ray and McDow (2005). All our ratios for succinate (medians in the range of 0.02 to 0.04) are substantially lower than those of Limbeck *et al*. (2001, 2005) and Ray and McDow (2005). For glutarate, our median back/front filter ratios are 0.07 for Hyytiälä and in the range of 0.21 to 0.26 for the other sites. Most of these ratios are substantially larger than our ratios for the other three DCAs. Yet, they are all lower than the average ratios of the studies of Limbeck *et al*. (2001, 2005) and Ray and McDow (2005). In these earlier studies, it was attempted to find a relationship between the extent of the sampling artifacts and the volatility of the DCAs, thereby using the vapour pressure as a measure of volatility. Ray and McDow (2005) studied the artifacts for three of the four DCAs studied by us (oxalic acid was not included in their study) and they found that their results, with average backup fractions of 45% for malonic acid and 35% for glutaric acid, were consistent with the higher vapour pressure of malonic acid compared with that of

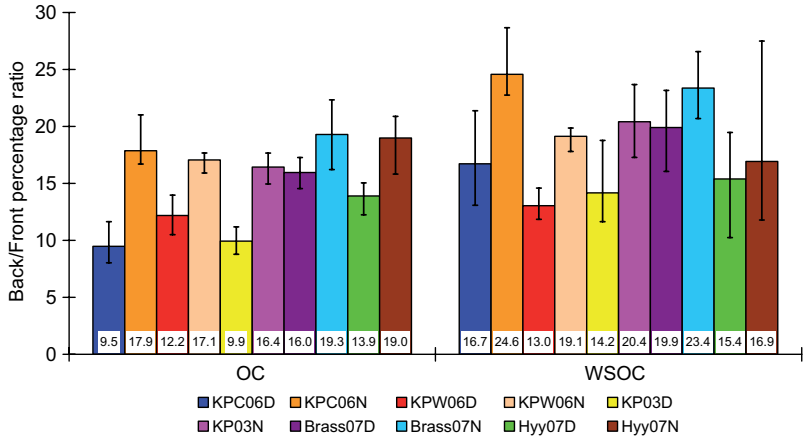

Fig. 1. Separate daytime and nighttime medians and interquartile ranges for the back/front filter percentage ratio for OC and WSOC in our several campaigns (KP stands for K-puszta; C for Cold period; W for Warm period; Brass for Brasschaat, Belgium; Hyy for Hyytiälä, Finland; D for daytime; N for nighttime).

glutaric acid, thereby referring to vapour pressure data determined by Bilde *et al*. (2003). Also their low average backup fraction of 15% for succinic acid was in line with this acid having the lowest vapour pressure of the three DCAs. In contrast, Limbeck *et al*. (2001, 2005) found no consistent relationship between backup fractions and vapour pressure and Limbeck *et al*. (2005) concluded that the gas/particle partition depends not only on the vapour pressure, but that also other physical and chemical processes influencing the gas phase to particle phase distribution have to be considered. Also in our data for the DCAs there is clearly no relationship between backup fraction and vapour pressure. Our median back/front filter percentage ratios increase in the following order: oxalate (1.5%)–succinate (3%)–malonate (2%–9%)–glutarate (7%–26%), whereas the vapour pressures for the solid DCAs and their saturated solutions, as recently provided by Soonsin *et al*. (2010), increase in the following order (with those for the solid DCA given in parentheses, in Pa): succinic acid (6.0×10^{-6})–glutaric acid (4.8×10^{-5})–malonic acid (8.0×10^{-5})–oxalic acid (2.5×10^{-4}).

Separate daytime and nighttime back/front filter ratios for $PM_{2.5}$ and investigation of the back/front filter ratio as a function of front filter loading

It was also examined to which extent the back/front filter ratios in our samplings differed between the daytime and nighttime. Incidentally, there was not much difference for the carbonaceous species between the daytime and nighttime concentrations derived from the front filters. For example, the ratios of the front filter median daytime to the front filter median nighttime concentration for OC were 1.06, 0.97, 1.00, 1.00, and 1.05 for the cold period of the 2006 campaign at K-puszta, the warm period of that campaign, the 2003 campaign at K-puszta, the 2007 campaign at Brasschaat, and the 2007 campaign at Hyytiääla, respectively. The corresponding ratios for oxalate were 0.84, 0.90, 0.87, 0.95, and 0.86 and those for succinate 1.05, 0.98, 1.09, 1.17, and 1.15. In contrast, for NO_3^- the ratios were 0.40, 0.39, 0.55, 0.44, and 0.99. The separate daytime and nighttime medians and interquartile ranges for the back/front ratio for OC and WSOC are shown in Fig. 1, whereas the data for oxalate and succinate are shown in Fig. 2. For NO_3^- (not shown) there was a clear tendency to have larger back/front ratios during the day. This is likely related to a higher fraction of the NO_3^- being present as gaseous HNO_3 during the day, as is also suggested by the lower daytime than nighttime front filter concentrations for NO_3^-. For both TC and WSOC (Fig. 1), the back/front ratios are systematically higher during the nighttime. Whether this means that the concentration ratios of the VOCs to particulate OC and of water-soluble VOCs to particulate WSOC are higher during the night than during the day seems rather implausible. It might indicate that a larger fraction of the VOCs and

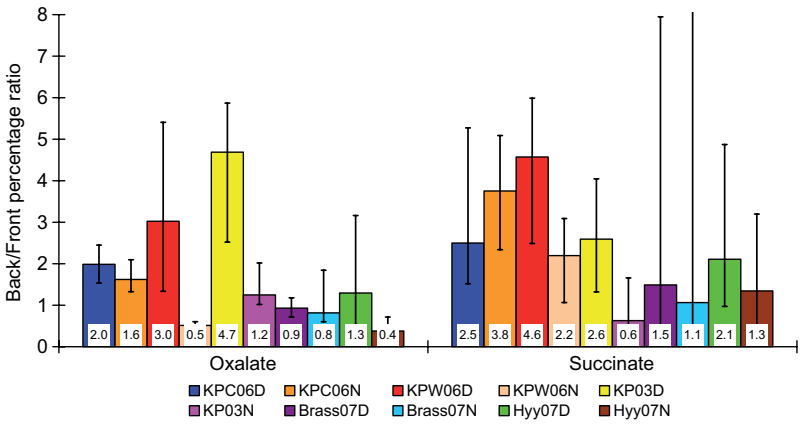

Fig. 2. Separate daytime and nighttime medians and interquartile ranges for the back/front filter percentage ratio for oxalate and succinate in our several campaigns (KP stands for K-puszta; C for Cold period; W for Warm period; Brass for Brasschaat, Belgium; Hyy for Hyytiälä, Finland; D for daytime; N for nighttime).

the water-soluble VOCs condense on the filters during the night because of the higher RH and consequently more humid filter fibres. For MSA^- (not shown) we had the same pattern as for OC and WSOC. In contrast, the DCAs oxalate and to a lesser extent also succinate exhibit higher back/front ratios in the daytime than in the night (Fig. 2). This might indicate that a larger fraction for these two DCAs was present in gaseous form during the warm day than during the cool night. For the other two DCAs (malonate and glutarate) no consistent picture was seen.

Ray and McDow (2005) found that the extent of artifact error was strongly dependent on apparent particulate concentration collected on the front filters. This was especially apparent for malonic acid. At the very lowest concentrations, below about 5 ng m^{-3}, backup fractions were often greater than 50% and occasionally greater than 100%, whereas at concentrations greater than 10 ng m^{-3}, backup fractions never exceeded 10%. They indicated that their results were consistent with observations of a nearly constant vapour adsorption artifact with a more variable ambient particulate organic carbon concentration. We investigated whether the same relationship as seen by Ray and McDow (2005) was also present in our data sets and we did this for malonate and succinate and also for OC and WSOC. No clear relationship was observed in our data, although it must be admitted that few front filter concentrations for malonate and succinate were below 5 ng m^{-3}. As an example of the relationships in our data sets, those for malonate and succinate in the 2006 K-puszta campaign are shown in Fig. 3.

Conclusions

It may be concluded that the sampling artifacts for the inorganic species in $PM_{2.5}$ in our HVDS samplings at three forested sites in Europe were small (< 5%) with the exception of those for nitrate. The sampling artifacts for MSA^- and the three major DCAs were also small (< 10%); they were clearly smaller than those for OC, TC, and especially WSOC. The artifacts for the DCAs at our sites were overall lower to much lower than those found in the studies of Limbeck *et al*. (2001, 2005) and Ray and McDow (2005). It is possible that the low sampling artifacts for MSA^- and the three major DCAs are due to the fact that these species were mainly present in the aerosol as salts instead of as acids. Especially methanesulphonic acid and oxalic acid, which are the strongest acids of the 5 organic acids reported in this study, are expected to have been mainly present as salts, considering the extent of neutralisation of the aerosol at our sites. The low back/front ratios for MSA^- and the three major DCAs indicate that a very small fraction of these compounds was present in the vapour phase. In contrast to Ray and McDow (2005) we found no clear relationship between backup fraction and front filter concentration for malonate and succinate. There was also no relationship at all between backup fraction and vapour pressure of the DCAs. This all indicates, as also concluded by Limbeck *et al*. (2005), that the gas/particle partition and filter sampling artifacts not only depend on the vapour pressure, but also on other physical and chemical processes. Bao *et al*.

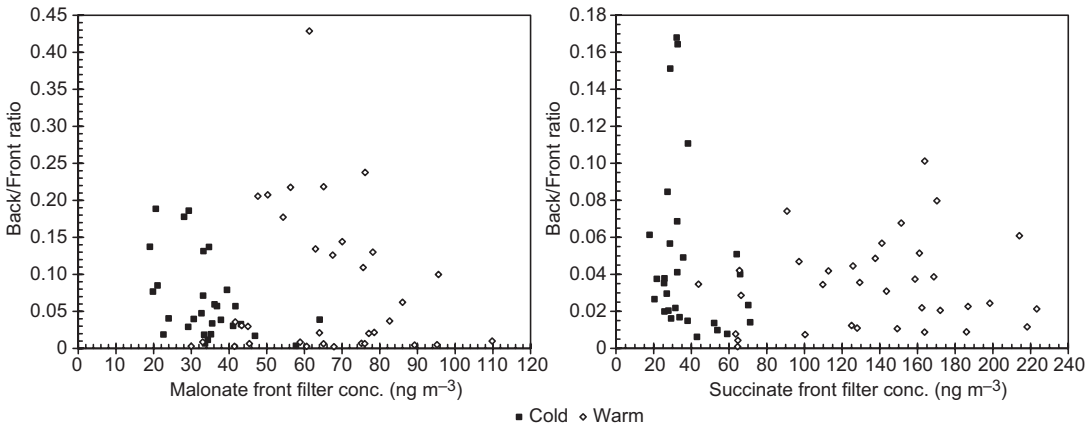

Fig. 3. Back/front filter ratio as a function of front filter concentration for malonate and succinate during the 2006 summer campaign at K-puszta.

(2011) indicated that the gas/particle partitioning of the diacids also depends on the characteristics of the atmosphere (e.g., temperature, sunlight and RH) and the aerosol (e.g., acidity, alkaline composition and water content). Measuring these characteristics in addition to measurements of both the gas-phase and particulate phase concentrations of the DCAs is therefore recommended in future studies. Besides, it is recommended to measure both the acidic and anionic forms of the DCAs in the aerosol, as done by Yang and Yu (2008).

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References

Abbatt J.P.D., Broekhuizen K. & Pradeep Kumar P. 2005. Cloud condensation nucleus activity of internally mixed ammonium sulfate/organic acid aerosol particles. *Atmos. Environ.* 39: 4767–4778.

Bao L., Matsumoto M., Kubota T., Kazuhiko S., Wang Q. & Sakamoto K. 2011. Gas/particle partitioning of low-molecular-weight dicarboxylic acids at a suburban site in Saitama, Japan. *Atmos. Environ.*, doi:10.1016/j.atmosenv.2009.09.014. [In press].

Bilde M., Svenningsson B., Mønster J. & Rosenørn T. 2003. Even-odd alternation of evaporation rates and vapor pressure of C3 to C9 dicarboxylic acids. *Environ. Sci. Technol.* 37: 1371–1378.

Birch M.E. & Cary R.A. 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. *Aerosol Sci. Technol.* 25: 221–241.

Chebbi A. & Carlier P. 1996. Carboxylic acids in the troposphere, occurrence, sources, and sinks: a review. *Atmos. Environ.* 30: 4233–4249.

Chi X. 2009. *Development of improved sampling and analysis methods for measuring organic, elemental, and water-soluble organic carbon in atmospheric aerosols and application to aerosol studies in Europe and tropical/equatorial and oceanic regions*. Ph.D. thesis, Ghent University.

Cruz C.N. & Pandis S.N. 1998. The effect of organic coatings on the cloud condensation nuclei activation of inorganic atmospheric aerosol. *J. Geophys. Res.* 103: 13111–13123.

Graedel T.E. & Keene W.C. 1995. Tropospheric budget of reactive chlorine. *Global Biogeochem. Cycles* 9: 47–77.

Ion A.C., Vermeylen R., Kourtchev I., Cafmeyer J., Chi X., Gelencsér A., Maenhaut W. & Claeys M. 2005. Polar organic compounds in rural $PM_{2.5}$ aerosols from K-puszta, Hungary, during a 2003 summer field campaign: sources and diel variations. *Atmos. Chem. Phys.*

5: 1805–1814.

Kawamura K., Kasukabe H. & Barrie L.A. 1996. Source and reaction pathways of dicarboxylic acids, ketoacids and dicarbonyls in arctic aerosols: one year of observations. *Atmos. Environ.* 30: 1709–1722.

Kawamura K., Yokoyama K., Fujii Y. & Watanabe O. 2001. A Greenland ice core record of low molecular weight dicarboxylic acids, ketocarboxylic acids, and α-dicarbonyls: a trend from Little Ice Age to the present (1540 to 1989 A.D.). *J. Geophys. Res.* 106: 1331–1345.

Kettle A.J. & Andreae M.O. 2000. Flux of dimethylsulfide from the oceans: A comparison of updated data sets and flux models. *J. Geophys. Res.* 105: 26793–26808.

Kulmala M., Hämeri K., Aalto P.P., Mäkelä J.M., Pirjola L., Nilsson E.D., Buzorius G., Rannik U., Dal Maso M., Seidl W., Hoffmann T., Jansson R., Hansson H.-C., Viisanen Y., Laaksonen A. & O'Dowd C.D. 2001. Overview of the international project on biogenic aerosol formation in the boreal forest (BIOFOR). *Tellus* 53B: 324–343.

Kourtchev I., Copolovici L., Claeys M. & Maenhaut W. 2009. Characterization of atmospheric aerosols at a forested site in central Europe. *Environ. Sci. Technol.* 43: 4665–4671.

Legrand M., Preunkert S., Galy-Lacaux C., Liousse C. & Wagenbach D. 2005. Atmospheric year-round records of dicarboxylic acids and sulfate at three French sites located between 630 and 4360 m elevation. *J. Geophys. Res.* 110, D13302, doi:10.1029/2004JD005515.

Lide D.R. (ed.) 2006. *CRC handbook of chemistry and physics*, 86th ed. (CDROM ver. 2006). Taylor and Francis, Boca Raton, FL.

Limbeck A., Puxbaum H., Otter L. & Scholes M.C. 2001. Semivolatile behavior of dicarboxylic acids and other polar organic species at a rural background site (Nylsvley, RSA). *Atmos. Environ.* 35: 1853–1862.

Limbeck A., Kraxner Y. & Puxbaum H. 2005. Gas to particle distribution of low molecular weight dicarboxylic acids at two different sites in central Europe (Austria). *J. Aerosol Sci.* 36: 991–1005.

Lupu A. & Maenhaut W. 2002. Application and comparison of two statistical trajectory techniques for identification of source regions of atmospheric aerosol species. *Atmos. Environ.* 36: 5607–5618.

Mader B.T., Schauer J.J., Seinfeld J.H., Flagan R.C., Yu J.Z., Yang H., Lim H.J., Turpin B.J., Deminter J.T., Heidemann G., Bae M.S., Quinn P., Bates T., Eatough D.J., Huebert B.J., Bertram T. & Howell S. 2003. Sampling methods used for the collection of particle-phase organic and elemental carbon during ACE-Asia. *Atmos. Environ.* 37: 1435–1449.

Maenhaut W., Claeys M., Janssens I. & Kulmala M. 2008a. *Formation mechanisms, marker compounds and source apportionment for BIOgenic atmospheric aeroSOLs (BIOSOL)*. Belgian Science Policy, Science for a Sustainable Development (SSD), Research Project SD/AT/02A, Final report Phase I.

Maenhaut W., Raes N., Chi X., Cafmeyer J. & Wang W. 2008b. Chemical composition and mass closure for PM2.5 and PM10 aerosols at K-puszta, Hungary, in summer 2006. *X-Ray Spectrom.* 37: 193–197.

Maenhaut W., Nava S., Lucarelli F., Wang W., Chi X. & Kulmala M. 2011. Chemical composition, impact from biomass burning, and mass closure for PM2.5 and PM10 aerosols at Hyytiälä, Finland, in summer 2007. *X-Ray Spectrom.* 40: 168–171.

Mäkelä J.M., Aalto P., Jokinen V., Pohja T., Nissinen A., Palmroth S., Markkanen T., Seitsonen K., Lihavainen H. & Kulmala M. 1997. Observations of ultrafine aerosol particle formation and growth in boreal forest. *Geophys. Res. Lett.* 24: 1219–1222.

Mkoma S.L. 2008. *Physico-chemical characterisation of atmospheric aerosols in Tanzania, with emphasis on the carbonaceous aerosol components and on chemical mass closure*. Ph.D. thesis, Ghent University.

Ocskay R., Salma I., Wang W. & Maenhaut W. 2006. Characterization and diurnal variation of size-resolved inorganic water-soluble ions at a rural background site. *J. Environ. Monit.* 8: 300–306.

Peng C., Chan M.N. & Chan C.K. 2001. The hygroscopic properties of dicarboxylic and multifunctional acids: measurements and UNIFAC predictions. *Environ. Sci. Technol.* 35: 4495–4501.

Pio C.A. & Lopes D.A. 1998. Chlorine loss from marine aerosol in a coastal atmosphere. *J. Geophys. Res.* 103: 25263–25272.

Pio C., Legrand M., Oliveira T., Afonso J., Santos C., Caseiro A., Fialho P., Barata F., Puxbaum H., Sanchez-Ochoa A., Kasper-Giebl A., Gelencsér A., Preunkert S. & Schock M. 2007. Climatology of aerosol composition (organic versus inorganic) at non-urban areas on a west-east transect across Europe. *J. Geophys. Res.* 112, D23S02, doi:10.1029/2006JD008038.

Putaud J.-P., Van Dingenen R., Alastuey A., Bauer H., Birmili W., Cyrys J., Flentje H., Fuzzi S., Gehrig R., Hansson H.C., Harrison R.M., Herrmann H., Hitzenberger R., Hüglin C., Jones A.M., Kasper-Giebl A., Kiss G., Kousa A., Kuhlbusch T.A.J., Löschau G., Maenhaut W., Molnar A., Moreno T., Pekkanen J., Perrino C., Pitz M., Puxbaum H., Querol X., Rodriguez S., Salma I., Schwarz J., Smolik J., Schneider J., Spindler G., ten Brink H., Tursic J., Viana M., Wiedensohler A. & Raes F. 2010. A European aerosol phenomenology — 3: physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. *Atmos. Environ.* 44: 1308–1320.

Ray J. & McDow S.R. 2005. Dicarboxylic acid concentration trends and sampling artifacts. *Atmos. Environ.* 39: 7906–7919.

Rogge W.F., Mazurek M.A., Hildemann L.M. & Cass G.R. 1993. Quantification of urban organic aerosols at a molecular level: identification, abundance and seasonal variation. *Atmos. Environ.* 27A: 1309–1330.

Salma I., Chi X. & Maenhaut W. 2004. Elemental and organic carbon in urban canyon and background environments in Budapest, Hungary. *Atmos. Environ.* 38: 27–36.

Salma I., Ocskay R., Chi X. & Maenhaut W. 2007. Sampling artefacts, concentration and chemical composition of fine water-soluble organic carbon and humic-like substances in a continental urban atmospheric environment.

Atmos. Environ. 41: 4106–4118.

Saltzman E.S., Savoie D.L., Zika R.G. & Prospero J.M. 1983. Methane sulfonic-acid in the marine atmosphere. *J. Geophys. Res.* 88: 897–902.

Schaap M., Spindler G., Schulz M., Acker K., Maenhaut W., Berner A., Wieprecht W., Streit N., Müller K., Brüggemann E., Chi X., Putaud J.-P., Hitzenberger R., Puxbaum H., Baltensperger U. & ten Brink H. 2004. Artefacts in the sampling of nitrate studied in the "INTERCOMP" campaigns of EUROTRAC-AEROSOL. *Atmos. Environ.* 38: 6487–6496.

Schwarz J., Chi X., Maenhaut W., Civiš M., Hovorka J. & Smolík J. 2008. Elemental and organic carbon in atmospheric aerosols at downtown and suburban sites in Prague. *Atmos. Res.* 90: 287–302.

Seinfeld J.H. & Pandis S.N. 1998. *Atmospheric chemistry and physics: from air pollution to climate change*. John Wiley & Sons, New York.

Solomon P.A., Moyers J.L. & Fletcher R.A. 1983. High-volume dichotomous virtual impactor for the fractionation and collection of particles according to aerodynamic size. *Aerosol Sci. Technol.* 2: 455–464.

Soonsin V., Zardini A.A., Marcolli C., Zuend A. & Krieger U.K. 2010. The vapor pressures and activities of dicarboxylic acids reconsidered: the impact of the physical state of the aerosol. *Atmos. Chem. Phys.* 10: 11753–11767.

Subramanian R., Khlystov A.Y., Cabada J.C. & Robinson A.L. 2004. Positive and negative artifacts in particulate organic carbon measurements with denuded and undenuded sampler configurations. *Aerosol Sci. Technol.* 38 (S1): 27–48.

Tang I.N. & Munkelwitz H.R. 1991. Determination of vapor-pressure from droplet evaporation kinetics. *J. Colloid Interface Sci.* 141: 109–118.

Turpin B.J., Saxena P. & Andrews E. 2000. Measuring and simulating particulate organics in the atmosphere: problems and prospects. *Atmos. Environ.* 34: 2983–3013.

Vecchi R., Valli G., Fermo P., D'Alessandro A., Piazzalunga A. & Bernardoni V. 2009. Organic and inorganic sampling artefacts assessment. *Atmos. Environ.* 43: 1713–1720.

Viana M., Chi X., Maenhaut W., Querol X., Alastuey A., Mikuška P. & Večeřa Z. 2006a. Organic and elemental carbon concentrations in carbonaceous aerosols during summer and winter sampling campaigns in Barcelona, Spain. *Atmos. Environ.* 40: 2180–2193.

Viana M., Chi X., Maenhaut W., Cafmeyer J., Querol X., Alastuey A., Mikuška P. & Večeřa Z. 2006b. Influence of sampling artefacts on measured PM, OC, and EC levels in carbonaceous aerosols in an urban area. *Aerosol Sci. Technol.* 40: 107–117.

Viana M., Maenhaut W., ten Brink H.M., Chi X., Weijers E., Querol X., Alastuey A., Mikuška P. & Večeřa Z. 2007. Comparative analysis of organic and elemental carbon concentrations in carbonaceous aerosols in three European cities. *Atmos. Environ.* 41: 5972–5983.

Yang L. & Yu L.E. 2008. Measurements of oxalic acid, oxalates, malonic acid, and malonates in atmospheric particulates. *Environ. Sci. Technol.* 42: 9268–9275.

Wang W. 2010. *Inorganic and organic speciation of atmospheric aerosols by ion chromatography and aerosol chemical mass closure*. Ph.D. thesis, Ghent University.

Wieprecht W., Acker K., Müller K., Spindler G., Brüggemann E., Maenhaut W., Chi X., Hitzenberger R., Bauer H. & ten Brink H. 2004. INTERCOMP2000: Ionic constitution and comparison of filter and impactor. *Atmos. Environ.* 38: 6477–6486.